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Perpendicular Magnetic Anisotropy and Hydrogenation-Induced Magnetic Change of Ta/Pd/CoFeMnSi/MgO/Pd Multilayers

Qing Zhang, Huarui Fu, Caiyin You*, Li Ma and Na Tian

Abstract

The perpendicular magnetic anisotropy (PMA) has been achieved in Ta/Pd/CoFeMnSi (CFMS)/MgO/Pd film, in which the Heusler compound CoFeMnSi is one of the most promising candidates for spin gapless semiconductor (SGS). The strong PMA, with the effective anisotropy constant K_{eff} of $5.6 \times 10^5 \text{ erg/cm}^3$ ($5.6 \times 10^4 \text{ J/m}^3$), can be observed in the Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at 300 °C. In addition, it was found that the magnetic properties of Ta/Pd/CFMS/MgO/Pd films are sensitive to hydrogen (H_2) under a weak magnetic field ($< 30 \text{ Oe}$), whose residual magnetization (M_r) decreased from 123.15 to 30.75 emu/cm^3 in the atmosphere with H_2 concentration of 5%.

Keywords: Spin gapless semiconductor, Perpendicular magnetic anisotropy, Hydrogenation-induced magnetic change

Background

Nowadays, hydrogen (H_2) as one of the new clean and efficient energy source has attracted more attentions, and thus, ensuring the safety of its usage becomes more and more significant. Solid state conductometric gas sensor is commonly used to detect the hydrogen, but it lacks the chemical selectivity and humidity sensitivity [1]. Recently, the magnetic sensors have been proved to be a useful way to detect the various gases, especial hydrogen, in which the film structures containing palladium (Pd) layer are currently under the intense study because the Pd possesses the high sensitivity [2] and selectivity [3] to hydrogen. Thus, the Pd-containing films can be used as an effective catalyst for hydrogen dissociation and absorption [4]. To date, many studies have reported the hydrogenation-induced magnetic change in Pd-rich magnetic alloy film and Pd/ferromagnetic layer (Pd/FM) multilayer films, such as $\text{Co}_{17}\text{Pd}_{83}$ [1], Pd/Fe [5], $[\text{Co}/\text{Pd}]_{12}$ [6], and Pd/Co/Pd [7] films. The hydrogenation-induced magnetic change can be attributed to the swell of Pd lattice due to the hydrogen absorption, which could contribute to about 2–3% volume expansion.

On the other hand, Pd as a noble metal is commonly used for realizing the perpendicular magnetic anisotropy

(PMA) owing to the d - d electron orbital hybridization at the interfaces of Pd/ferromagnetic layer. This critical interfacial effect of electron orbital hybridization is very sensitive to the interfacial strain or stress [8], which could be brought in through the volume evolution of noble metal. Therefore, high sensitivity of hydrogen-induced magnetic change could be expected from the PMA film with Pd layer by making use of the strong interfacial dependences of perpendicular magnetic anisotropy.

So far, a huge number of studies of PMA have been reported, which have been originated from the d - d or d - p electron orbital hybridizations of ferromagnetic layer and noble metal (Pt, Pd) or oxygen of oxides at the interfaces [9–12]. Moreover, Heusler quaternary compound CoFeMnSi (CFMS) has been proved to be a spin gapless semiconductor (SGS) [13–15], which is also very sensitive to the external field [16], showing the potential advantages of being a sensor. In this work, the Ta/Pd/CoFeMnSi/MgO/Pd-structured films were designed to achieve the strong PMA by the interfacial effect, and the hydrogenation-induced magnetic change was explored. Different from the above reports [1, 5–7], the perpendicular magnetic anisotropic film structure and SGS-like CoFeMnSi ferromagnetic layer are all sensitive to the extrinsic effects, such as interfacial stress or strain. Thus, the highly

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sensitive change of magnetism could be expected from the films under a low magnetic field.

Methods

Four sets of samples were prepared as follows: Ta (6 nm)/Pd (2.4 nm)/CoFeMnSi (2.3 nm)/MgO (t_{MgO})/Pd (2 nm) ($t_{\text{MgO}} = 0.9\text{--}1.5$ nm) (hereinafter refer to Ta/Pd/CFMS (2.3 nm)/MgO (t_{MgO})/Pd), Ta (6 nm)/Pd (2.4 nm)/CoFeMnSi (t_{CFMS})/MgO (1.3 nm)/Pd (2 nm) ($t_{\text{CFMS}} = 1.9\text{--}3.1$ nm) (hereinafter refer to Ta/Pd/CFMS (t_{CFMS})/MgO (1.3 nm)/Pd), Ta (6 nm)/Pd (2.4 nm)/CoFeMnSi (2.3 nm)/Pd (2 nm) (hereinafter refer to Ta/Pd/CFMS/Pd), and Ta (6 nm)/CoFeMnSi (2.3 nm)/MgO (1.3 nm)/Pd (2 nm) (hereinafter refer to Ta/CFMS/MgO/Pd). All films were deposited on the Si substrate by magnetron sputtering system under a base pressure better than 2.6×10^{-5} Pa at room temperature. The purity of CoFeMnSi target was better than 99.9%. The CFMS layer was deposited under Ar pressure of 0.9 Pa with the DC power of 40 W. The MgO layer was deposited under Ar pressure of 0.2 Pa with the RF power of 150 W. The Ta layer was deposited under Ar pressure of 0.3 Pa with the DC power of 50 W, and Pd layer was deposited under Ar pressure of 0.3 Pa with the DC power of 25 W. The films were annealed within the temperature range from 250 to 450 °C for 30 min under a vacuum chamber below 10^{-4} Pa.

The magnetic properties were characterized by vibrating sample magnetometer (VSM: Lakeshore 7404). The electric transport property measurement system

(ET Chen, ET9000) was used to monitor the Hall resistivity with the change of hydrogen absorption and desorption in real time. All measurements were carried out at room temperature and atmospheric pressure. The total gas flow rate was fixed at 3.5 L/min for the sensitivity of hydrogen gas. The hydrogen concentration was tuned by controlling the gas flow rate of the mixed gas ($\text{H}_2\text{:Ar} = 5\text{:95}$) and nitrogen gas (N_2).

Results and Discussion

To understand the effect of the MgO layer thickness on PMA, Fig. 1 shows magnetic hysteresis loops measured along the in-plane and out-of-plane directions for Ta/Pd/CFMS (2.3 nm)/MgO (t_{MgO})/Pd films annealed at 300 °C with varied thicknesses t_{MgO} . All samples are easily magnetized along the out-of-plane direction, and large saturation fields are needed along the in-plane direction, exhibiting PMA behaviors. The strength of PMA firstly increases with increasing t_{MgO} and reaches the maximum value with the squareness (M_r/M_s) close to 1 when $t_{\text{MgO}} = 1.3$ nm while obviously decreases with further increasing t_{MgO} .

In order to elucidate the influence of annealing temperature on PMA, Fig. 2 shows the M-H loops of the Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at different temperatures (250–450 °C). The as-deposited sample exhibits an in-plane magnetic anisotropy (IMA) as seen in Fig. 2a. Magnetic anisotropy did not change after annealing at a low temperature of

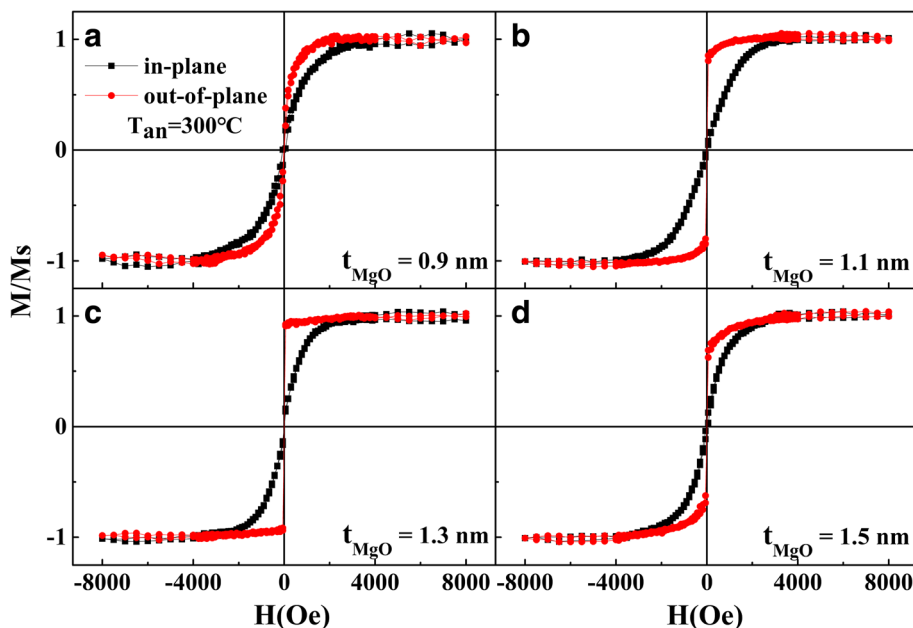


Fig. 1 In-plane and out-of-plane M-H loops of Ta/Pd/CFMS (2.3 nm)/MgO (t_{MgO})/Pd annealed at 300 °C. **a** $t_{\text{MgO}} = 0.9$ nm. **b** $t_{\text{MgO}} = 1.1$ nm. **c** $t_{\text{MgO}} = 1.3$ nm. **d** $t_{\text{MgO}} = 1.5$ nm

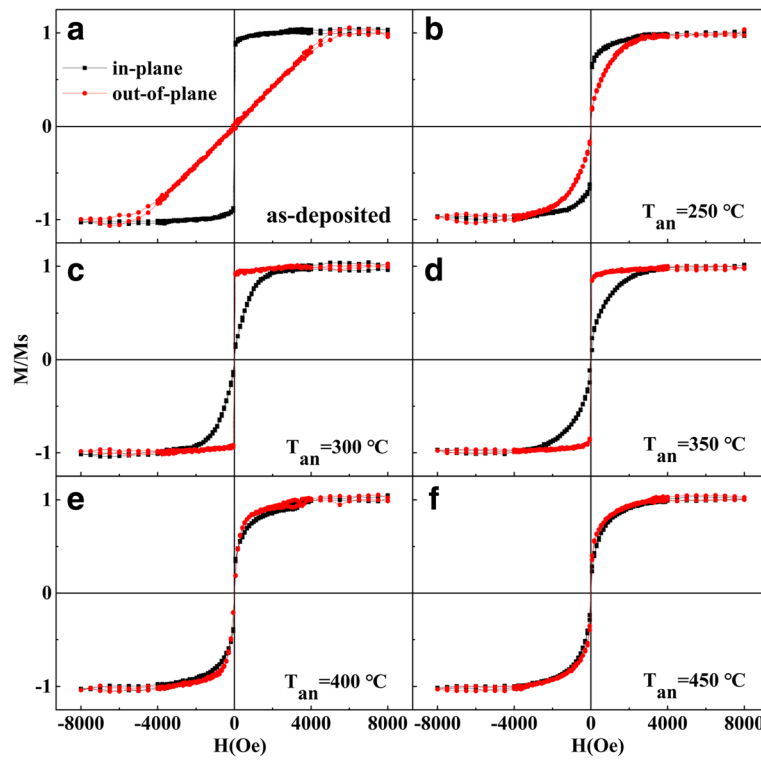


Fig. 2 In-plane and out-of-plane M-H loops of the Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at different temperatures. **a** As-deposited. **b** 250 °C. **c** 300 °C. **d** 350 °C. **e** 400 °C. **f** 450 °C

250 °C (Fig. 2b). The easy magnetization axis of the sample annealed at 300 °C shifted to out-of-plane direction, showing strong PMA (Fig. 2c). The PMA could be maintained after T_{an} rising to 350 °C, but the squareness decreased. With further increasing the T_{an} , the PMA was destroyed and the easy magnetization axis shifted back to in-plane orientation (Fig. 2e, f). The results indicate that the strong PMA can only be achieved at the proper annealing temperature and is easy to be deteriorated at a higher annealing temperature. This is because high annealing temperature could give rise to the intensified inter-diffusion of the atoms at the interface and deteriorate the electron orbital hybridization, which is consistent with our previous reports [9, 12, 17, 18].

In order to clarify the interfacial effect on the PMA in the Ta/Pd/CFMS/MgO/Pd films, the M-H loops of different film stacks were given in Fig. 3a–c. As shown in Fig. 3a, the film without MgO layer presents strong IMA behavior. But for the film without the bottom Pd layer, the easy magnetization axis of the Ta/CFMS/MgO/Pd sample exhibits a slight shift from the in-plane direction, showing the weak IMA (Fig. 3b). The strong PMA is observed in the film after inserting the Pd and MgO layers (i.e., Ta/Pd/CFMS/MgO/Pd) as seen in Fig. 3c, implying that both the Pd/CFMS and CFMS/MgO interface are essential for realizing PMA, and the contribution of

CFMS/MgO interface to the PMA plays a major role [12, 17]. That is, an appropriate amount of Co-O bonds at the CFMS/MgO interface is helpful for achieving the optimum PMA. The thin MgO layer makes CFMS/MgO underoxidized (Fig. 1a, b), and thick MgO layer makes CFMS/MgO overoxidized (Fig. 1d), which both weaken the PMA [11]. As shown in Fig. 1c, the sample with $t_{MgO} = 1.3$ nm has the proper Co-O bonds in the CFMS/MgO interface to obtain strong PMA.

To quantify the PMA strength in the Ta/Pd/CFMS/MgO/Pd films, the effective anisotropy constant K_{eff} is given by

$$K_{eff} = K_V - 2\pi M_S^2 + K_S/t_{CFMS} \quad (1)$$

where K_V and K_S are the bulk and interface anisotropy, respectively. K_{eff} is determined by the differences of magnetization energy between the hard and easy magnetization directions. The positive K_{eff} represents PMA, and the negative K_{eff} represents IMA. The product of $K_{eff} \times t_{CFMS}$ as a function of t_{CFMS} for the Ta/Pd/CFMS (t_{CFMS})/MgO (1.3 nm)/Pd films annealed at different temperatures is shown in Fig. 3d. All as-deposited films present the negative K_{eff} , implying the absence of PMA. The PMA of the films annealed at 250 °C can only be observed with $t_{CFMS} = 1.9$ nm. For the films annealed

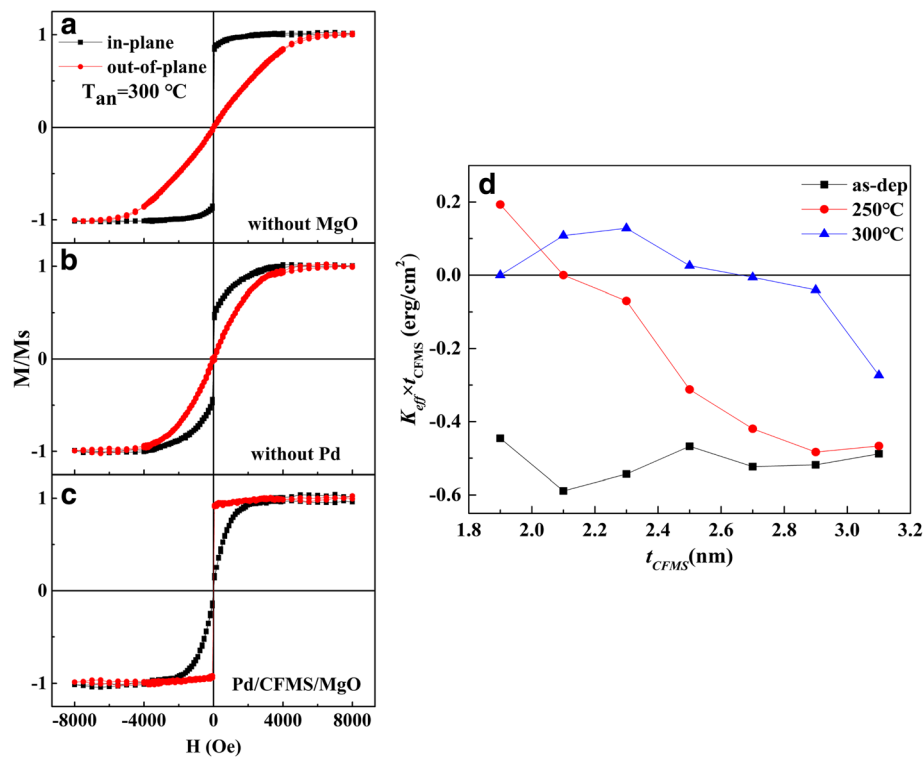


Fig. 3 The M-H loops of **a** Ta/Pd/CFMS/Pd, **b** Ta/CFMS/MgO/Pd, and **c** Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd annealed at 300 °C and **d** the CFMS layer thickness dependence of $K_{\text{eff}} \times t_{\text{CFMS}}$ product for Ta/Pd/CFMS (t_{CFMS})/MgO (1.3 nm)/Pd annealed at different temperatures

at 300 °C, the PMA can be maintained within a wide t_{CFMS} range (below 2.7 nm). The largest K_{eff} value of the sample is 5.6×10^5 erg/cm³ (5.6×10^4 J/m³) with $t_{\text{CFMS}} = 2.3$ nm.

As shown above, the PMA is very sensitive to the interfacial environment, which could be also affected through the gas absorption or desorption of noble metal Pd. Thus, the hydrogenation-induced magnetic change was investigated on the Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at 300 °C. The M-H loops were checked under different gas atmospheres through varying the H₂ concentration as shown in Fig. 4a. Noted here, the M-H loops cannot be affected by the pure nitrogen N₂ and pure argon Ar atmospheres (data did not show here). After introducing H₂, the M-H loop significantly changes, and the easy magnetization axis shifts away from the out-of-plane direction, showing a large saturation field of the out-of-plane magnetic curve. It is found that the saturation field increases with increasing H₂ concentration. The sample exhibits an excellent hydrogen sensitivity under a small applied magnetic field (< 30 Oe). Figure 4b shows the M-H loops measured under the air atmosphere before and after the addition of H₂. It can be seen that the M-H loop is well back to the initial state after removing H₂. As shown in Fig. 4c, M_r decreases from

123.15 to 30.75 emu/cm³ (decreased 75%), and the saturation field (H_k) increases from 5.5 to 18 Oe with increasing H₂ concentration from 0 to 5%.

Figure 5 shows the dependence of the Hall resistivity on time for H₂ absorption and desorption in Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd annealed at 300 °C. As shown in Fig. 5, H₂ absorption rate is faster than the desorption rate. The Hall resistivity gradually increased to be saturated in 70 min after being exposed to H₂. However, through introducing N₂ to expel H₂, the Hall resistivity only decreases 60% due to undesorbed H₂. The Hall resistivity increased/decreased quickly at the beginning (first 10 min) under the processes of H₂ absorption/desorption, since the hall resistivity is mainly related to the magnetic layer (CoFeMnSi). Thus, it can be deduced that the resistivity changes at the beginning are majorly originated from the interfacial variations between Pd and CoFeMnSi layers due to H₂ absorption/desorption. The resistivity change at the later stage could be the intrinsic changes of multilayer films due to the absorbed H₂. In comparison to Fig. 4b, the magnetic detection of multilayered films could be very reproducible owing to the well recovering of the magnetic performance in comparison to the resistivity variations.

As mentioned above, the hydrogenation-induced magnetic change mainly comes from the stress acting on the

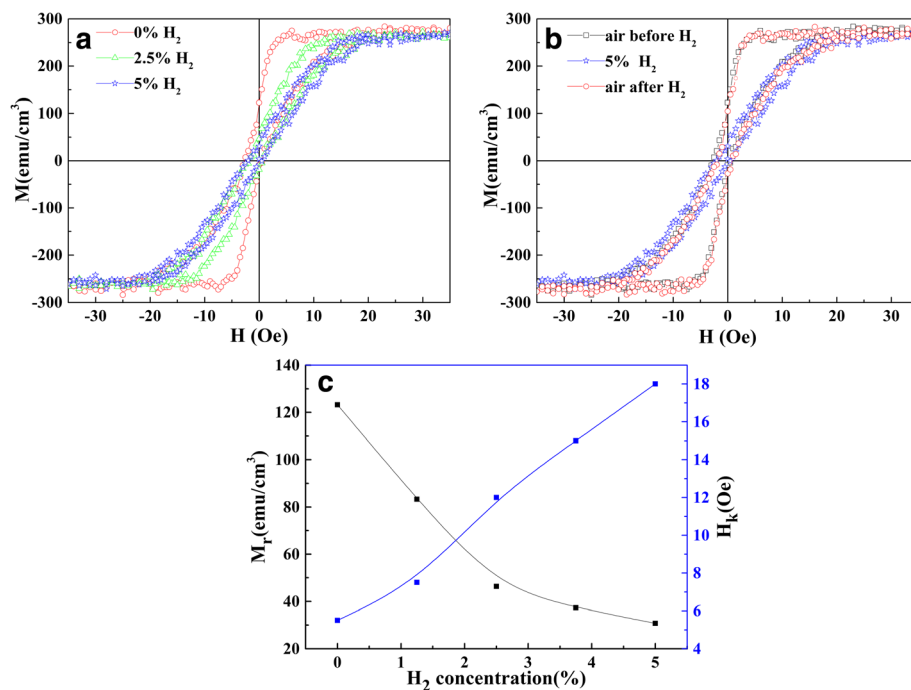


Fig. 4 The out-of-plane M-H loops for Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at 300 °C. **a** Under H₂ introduction. **b** Comparison after removing H₂. **c** The dependence of M_r and H_k on H₂ concentration

film with H₂ absorption of Pd in the Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd film system [19]. It is known that Pd is an effective catalyst for dissociating the hydrogen molecule [4]. Hydrogen molecules are adsorbed and dissociated to hydrogen atoms on the surface of the Pd layer. The lattice of Pd could be expanded with the absorption of hydrogen atoms [20], which in turn has tensile stress to its adjacent MgO and CFMS layer, leading to the controllable magnetism of CoFeMnSi. After

discharging H₂, the hydrogen atoms can escape from the Pd membrane surface [21], causing the recovering of the magnetic performance.

Conclusions

We demonstrated the strong PMA and the hydrogenation-induced magnetic change in the Ta/Pd/CFMS/MgO/Pd films. The loop squareness (M_r/M_s) is close to 1 for the sample with $t_{\text{CFMS}} = 2.3$ nm and $t_{\text{MgO}} = 1.3$ nm after annealing at 300 °C, obtaining a high perpendicular magnetic anisotropy K_{eff} value of 5.6×10^5 erg/cm³. Owing to the hydrogen absorption of Pd, the annealed Ta/Pd/CFMS/MgO/Pd film at 300 °C exhibited excellent hydrogen sensitivity; the residual magnetization (M_r) decreased 75% under the atmosphere with H₂ of 5%.

Abbreviations

CFMS: CoFeMnSi; IMA: In-plane magnetic anisotropy; PMA: Perpendicular magnetic anisotropy

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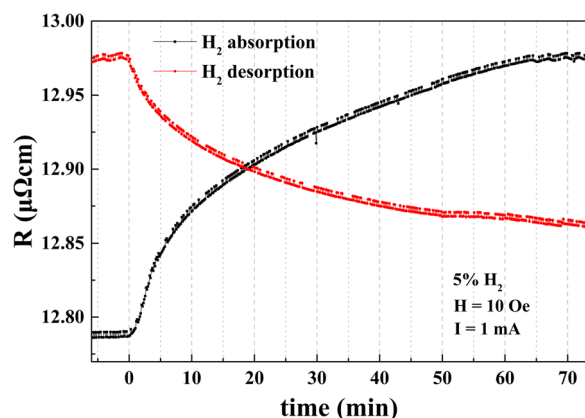


Fig. 5 The dependence of the Hall resistivity on time under H₂ absorption and desorption for Ta/Pd/CFMS (2.3 nm)/MgO (1.3 nm)/Pd films annealed at 300 °C

Availability of Data and Materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Authors' Contributions

QZ carried out the experiments and drafted the manuscript. HRF participated in the measurements and performed the analysis. CY supervised the overall study and polished the manuscript. LM and NT participated in the measurements. All the authors read and approved the final manuscript.

Competing Interests

The authors declare that they have no competing interests.

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